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(54) **DENTAL PRIMER COMPOSITION AND POLYMERIZATION CATALYST**

(57) There is provided a dental primer composition capable of obtaining high adhesive strength to both dentin and enamel, as a pretreatment material for a chemically polymerizable adhesive. This composition is a dental primer composition comprising a polymerizable monomer containing an acidic group, water, aryl borate and transition metal compound.

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Description

[Technical field of the Invention]

5 This invention relates to a dental primer composition and a polymerization catalyst. More specifically, it relates to a dental primer composition for firmly bonding a crown repairing material such as a composite resin, metal or ceramic to a tooth in a dental treatment field and to a polymerization catalyst useful particularly for this purpose.

[Background of Technique]

10 To repair the tooth damaged by dental caries or accident, a crown repair material such as a composite resin, metal, ceramic or the like is bonded to the tooth by an adhesive. As the adhesive for bonding a crown repair material to the tooth, there are currently available optically polymerizable adhesives and chemically polymerizable adhesives which are used depending on the type of a crown material. For example, an optically curable bonding material is used for
 15 repairing using optically curable composite resins, while a resin cement which is a chemically polymerizable adhesive is used for repairing using metal casts and ceramics.

The adhesive is required to keep a crown repair material being firmly bonded to the tooth for a long time in such a severe environment as the oral cavity. If the adhesive strength of the adhesive is low or the durability of the adhesive is insufficient, the repair material may fall off, or a gap may be produced between the tooth and the repair material with
 20 the result that bacteria may enter the gap, causing secondary dental caries.

The hard tissue of a tooth consists of enamel and dentin and a crown repair material is required to be bonded to both enamel and dentin clinically. Heretofore, to improve adhesion, the surface of a tooth has been pretreated prior to the application of an adhesive. A material for this pretreatment is generally an acidic aqueous solution for demineralizing the surface of a tooth, such as an aqueous solution of phosphoric acid, maleic acid or citric acid. In the case of
 25 enamel, the adhesion mechanism to the treated surface is mechanical macroscopic retention produced when an adhesive permeates the surface that has been made rough by demineralizing with an acidic aqueous solution, and hardens. Thereby, sufficient adhesive strength is obtained clinically. On the other hand, in the case of dentin, the adhesion mechanism is mechanical microscopic retention produced when an adhesive infiltrates into micro voids of a sponge-like collagen fiber exposed to the surface of a tooth after demineralizing, and hardens. However, since the infiltration of the
 30 adhesive into the exposed collagen layer is not easy, a generally called primer which is a permeation accelerating material is used and hence, operation becomes complicated.

To cope with this problem, for the purpose of simplifying bonding operation, a primer for the simultaneous pretreatment of both enamel and dentin has been studied. Japanese Laid-open Patent Publication Hei 3-240712 discloses a primer composition comprising a polymerizable monomer containing an acidic group, a polymerizable monomer containing a hydroxyl group, water and a curing material; Japanese Laid-open Patent Publication Hei 4-8368 a primer composition comprising a polymerizable monomer containing an acidic group, a polymerizable monomer containing a hydroxyl group, water and an amino compound having an acid group; Japanese Laid-open Patent Publication Hei 6-192029 discloses a pretreatment material comprising vinyl phosphonic acid, vinyl phosphonic acid metal salt, carboxylic acid having a hydrophobic group, water and alcohol; Japanese Laid-open Patent Publication Hei 6-192030 a pretreatment material comprising an organic sulfonic acid metal salt, organic carboxylic acid having a hydrophobic group, water and alcohol; Japanese Laid-open Patent Publication Hei 7-82115 a primer composition comprising a vinyl compound having an acidic group, a vinyl compound having a hydroxyl group, water, aromatic sulfonic acid and amine; Japanese Laid-open Patent Publication Hei 7-89820 a primer composition comprising a polymerizable monomer having an acidic group, water and a compound having an amide group and a hydroxyl group in the molecule; and Japanese Laid-open Patent Publication Hei 7-97306 a primer comprising a polymerizable monomer having an acidic group, an organic solvent and water as well as an adhesive system in which a curable composition comprising a polymerizable monomer having an acidic group, a polymerizable monomer having a hydroxyl group and a polymerization initiator are used.

However, when an optically curable adhesive such as a bonding material for composite resins or the like is used, all of the above compositions have adhesive force to both enamel and dentin. However, when a chemically polymerizable adhesive such as resin cement or the like is used, the compositions cannot necessarily have sufficient adhesive force yet. Chemically polymerizable adhesives generally have a lower rate of polymerization than optically polymerizable adhesives and hence, are inferior in adhesive strength. When trialkyl boron (or partial oxide thereof) which has high catalytic activity among the chemically polymerizable adhesives is used, high adhesive strength can be obtained, but it is necessary to separately keep the catalyst from a polymerizable compound before use because the catalyst is chemically unstable. Or rather, therefore, it involves a drawback that operation becomes complicated.

55 To cope with this problem, not only when an optically polymerizable adhesive is used but also when a chemically polymerizable adhesive is used, the development of a pretreatment material which can gain excellent adhesive strength has been desired.

[Disclosure of the Invention]

It is an object of the present invention to provide a novel dental primer composition.

It is another object of the present invention to provide a primer composition with which high adhesive strength to both dentin and enamel can be obtained by a single operation when it is applied to the surface of tooth irrespective of a chemically polymerizable adhesive or an optically polymerizable adhesive.

It is a further object of the present invention to provide a novel polymerization catalyst, particularly a polymerization catalyst advantageously used for a polymerizable monomer or a composition containing the same, such as a dental primer composition; and a catalyst component thereof.

Other objects and advantages of the present invention will become apparent from the following description.

The inventors of the present invention have conducted intensive studies to attain the above objects and advantages, and have found that when an aryl borate and a transition metal compound are used as polymerization catalyst components for a dental primer composition, the dental primer composition provides high adhesive strength to both enamel and dentin not only when an optically polymerizable adhesive is used but also when a chemically polymerizable adhesive is used. This finding has led to the present invention.

That is, the above objects and advantages of the present invention can be firstly attained by a dental primer composition comprising (A) a polymerizable monomer containing an acidic group, (B) water, (C) an aryl borate and (D) a transition metal compound.

The polymerizable monomer containing an acidic group (A) used in the dental primer composition or dental primer of the present invention contains at least one acidic group such as carboxylic acid group, phosphoric acid group, sulfonic acid group or phosphonic acid group in one molecule. The polymerizable monomer preferably contains, as a polymerizable group, at least one radical polymerizable unsaturated group such as acryloyl group, methacryloyl group, styryl group, vinyl group or aryl group in one molecule.

The polymerizable monomer containing a carboxylic acid group out of the above polymerizable monomers containing an acidic group preferably includes a monocarboxylic acid, dicarboxylic acid, tricarboxylic acid or tetracarboxylic acid. Examples thereof are (meth)acrylic acid, maleic acid, p-vinylbenzoic acid, 11-(meth)acryloyloxy-1,1-undecanedicarboxylic acid, 2-methacryloyloxyethyl 3'-methacryloyloxy-2'(3,4-dicarboxybenzoyloxy)propyl succinate (MTS), 2-methacryloyloxyethyl hydrogen malate, 1,4-di(meth)acryloyloxymethylpyromellitic acid, 6-(meth)acryloyloxyethylnaphthalene-1,2,6-tricarboxylic acid, 4-(meth)acryloyloxymethyltrimellitic acid and an anhydride thereof, 4-(meth)acryloyloxyethyltrimellitic acid, 4-(meth)acryloyloxybutyltrimellitic acid and an anhydride thereof, 4-[2-hydroxy-3-(meth)acryloyloxy]butyltrimellitic acid and an anhydride thereof, 2,3-bis(3,4-dicarboxybenzoyloxy)propyl (meth)acrylate, N,O-di(meth)acryloyloxytyrosine, O-(meth)acryloyloxytyrosine, N-(meth)acryloyloxytyrosine, N-(meth)acryloyl-p-aminobenzoic acid, N-(meth)acryloyl O-aminobenzoic acid, N-(meth)acryloyl 5-aminosalicylic acid, N-(meth)acryloyl 4-aminosalicylic acid, 2-, 3- or 4-(meth)acryloyloxybenzoic acid, addition product of 2-hydroxyethyl (meth)acrylate and pyromellitic dianhydride, 2-(3,4-dicarboxybenzoyloxy)-1,3-di(meth)acryloyloxypropane, 4-[(2-hydroxy-3-(meth)acryloyloxypropyl)amino]phthalic acid, 3 or 4-[N-methyl-N-(2-hydroxy-3-(meth)acryloyloxypropyl)amino]phthalic acid and the like. Out of these, the preferred are dicarboxylic acids and the more preferred are 11-methacryloyloxy-1,1-undecanedicarboxylic acid (MAC-10), 2-methacryloyloxyethyl 3'-methacryloyloxy-2'(3,4-dicarboxybenzoyloxy)propyl succinate (MTS), 4-methacryloyloxyethyltrimellitic anhydride (4-META), 4-acryloyloxyethyltrimellitic acid (4-AET), and the like.

Examples of the polymerizable monomer containing a phosphoric acid group include 2-(meth)acryloyloxyethyl dihydrogen phosphate, 2-(meth)acryloyloxyethyl acid phosphate, 2 or 3-(meth)acryloyloxypropyl acid phosphate, 4-(meth)acryloylbutyl acid phosphate, 6-(meth)acryloyloxybutyl acid phosphate, 8-(meth)acryloyloxydecyl acid phosphate, 10-(meth)acryloyloxydecyl acid phosphate, 12-(meth)acryloyloxydodecyl acid phosphate, bis[2-(meth)acryloyloxyethyl]acid phosphate, bis[2-(meth)acryloyloxyethyl]hydrogen phosphate, 2-(meth)acryloyloxyethylphenyl acid phosphate (phenyl-P), 2-(meth)acryloyloxyethyl-p-ethoxyphenyl acid phosphate, and the like. Compounds obtained by substituting a thiophosphoric acid group for the phosphoric acid group of these compounds are also included. Out of these compounds, 2-methacryloyloxyethyl dihydrogen phosphate, 2-(meth)acryloyloxyethylphenyl acid phosphate and the like are preferred.

Further, examples of the polymerizable monomer containing a sulfonic acid group include 2-sulfoethyl (meth)acrylate, 2-methyl-2-(meth)acrylamidepropanesulfonic acid, 2 or 1-sulfo-1 or 2-propyl (meth)acrylate, 1 or 3-sulfo-2-butyl (meth)acrylate, 3-bromo-2-sulfo-2-propyl (meth)acrylate, 3-methoxy-1-sulfo-2-propyl (meth)acrylate, 1,1-dimethyl-2-sulfoethyl (meth)acrylamide, 3-methoxy-1-sulfo-2-propyl (meth)acrylate, and the like. Out of these, 2-methyl-2-(meth)acrylamidepropanesulfonic acid is preferred.

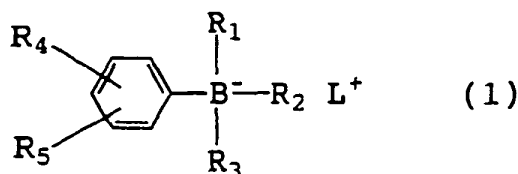
A typical example of phosphonic acid is vinyl phosphonic acid.

These polymerizable monomers containing an acidic group may be used in combination of plural monomers as required.

Out of the above polymerizable monomers containing an acidic group, polymerizable monomers containing a carboxylic acid group and polymerizable monomers containing a phosphoric acid group are preferred because they are excellent in adhesion to tooth. A use in combination of these monomers is more preferred.

Water as the component (B) contained in the dental primer of the present invention is used to demineralize the tooth and preferably contains substantially no impurities which impair storage stability, bio adaptability and adhesion. Demineralized water and distilled water are advantageously used as the water.

The aryl borate as the component (C) contained in the dental primer composition of the present invention has in one molecular at least one aryl group and boron which are directly bonded to each other and is preferably represented by the following general formula (1):



wherein R_1 , R_2 and R_3 are the same or different and each an alkyl group, alkenyl group, alkynyl group, aryl group, aralkyl group or alkaryl group and may be substituted, R_4 and R_5 are the same or different and each a hydrogen atom, halogen atom, alkyl group which may be substituted or aryl group which may be substituted, and L^+ is a metal ion, quaternary ammonium salt, quaternary pyridinium ion, quaternary quinolinium ion or phosphonium ion.

Since aryl borates having no boron-aryl bond are extremely unstable in shelf life storage and easily decompose by reacting with oxygen contained in air, they cannot be used as a surface treatment agent for the tooth.

Specific examples of the aryl borate suitably usable include aryl borates having one aryl group in one molecule, such as sodium salts, lithium salts, potassium salts, magnesium salts, tetrabutyl ammonium salts, tetramethyl ammonium salts, tetraethyl ammonium salts, methylpyridinium salts, ethylpyridinium salts, butylpyridinium salts, methylquinolinium salts, ethylquinolinium salts and butylquinolinium salts of trialkylphenylboron, trialkyl(p-chlorophenyl)boron, trialkyl(p-fluorophenyl)boron, trialkyl(p-methoxyphenyl)boron, trialkyl(m-methoxyphenyl)boron, trialkyl(p-ethoxyphenyl)boron, trialkyl(m-ethoxyphenyl)boron, trialkyl(p-butoxyphenyl)boron, trialkyl(m-butoxyphenyl)boron, trialkyl(p-methylphenyl)boron, trialkyl(m-methylphenyl)boron, trialkyl(p-ethylphenyl)boron, trialkyl(m-ethylphenyl)boron, trialkyl(p-butylphenyl)boron, trialkyl(m-butylphenyl)boron, trialkyl(3,5-bistrifluoromethyl)phenylboron and trialkyl[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]boron (hereinafter, the alkyl group is n-butyl, n-octyl, n-dodecyl or the like).

Examples of the aryl borate having two aryl groups in one molecule include sodium salts, lithium salts, potassium salts, magnesium salts, tetrabutyl ammonium salts, tetramethyl ammonium salts, tetraethyl ammonium salts, methylpyridinium salts, ethylpyridinium salts, butylpyridinium salts, methylquinolinium salts, ethylquinolinium salts and butylquinolinium salts of dialkyldiphenylboron, dialkyldi(p-chlorophenyl)boron, dialkyldi(p-fluorophenyl)boron, dialkyldi(p-methoxyphenyl)boron, dialkyldi(m-methoxyphenyl)boron, dialkyldi(p-ethoxyphenyl)boron, dialkyldi(m-ethoxyphenyl)boron, dialkyldi(p-butoxyphenyl)boron, dialkyldi(m-butoxyphenyl)boron, dialkyldi(p-methylphenyl)boron, dialkyldi(m-methylphenyl)boron, dialkyldi(p-ethylphenyl)boron, dialkyldi(m-ethylphenyl)boron, dialkyldi(p-butylphenyl)boron, dialkyldi(m-butylphenyl)boron, dialkyldi(3,5-bistrifluoromethyl)phenylboron and dialkyldi[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]boron (hereinafter, alkyl group is n-butyl, n-octyl, n-dodecyl or the like).

Examples of the aryl borate having three aryl groups in one molecule include sodium salts, lithium salts, potassium salts, magnesium salts, tetrabutyl ammonium salts, tetramethyl ammonium salts, tetraethyl ammonium salts, methylpyridinium salts, ethylpyridinium salts, butylpyridinium salts, methylquinolinium salts, ethylquinolinium salts and butylquinolinium salts of monoalkyltriphenylboron, monoalkyltri(p-chlorophenyl)boron, monoalkyltri(p-fluorophenyl)boron, monoalkyltri(p-methoxyphenyl)boron, monoalkyltri(m-methoxyphenyl)boron, monoalkyltri(p-ethoxyphenyl)boron, monoalkyltri(m-ethoxyphenyl)boron, monoalkyltri(p-butoxyphenyl)boron, monoalkyltri(m-butoxyphenyl)boron, monoalkyltri(p-methylphenyl)boron, monoalkyltri(m-methylphenyl)boron, monoalkyltri(p-ethylphenyl)boron, monoalkyltri(m-ethylphenyl)boron, monoalkyltri(p-butylphenyl)boron, monoalkyltri(m-butylphenyl)boron, monoalkyltri(3,5-bistrifluoromethyl)phenylboron and monoalkyltri[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]boron (hereinafter, alkyl group is n-butyl, n-octyl, n-dodecyl or the like).

Examples of the aryl borate having four aryl groups in one molecule include sodium salts, lithium salts, potassium salts, magnesium salts, tetrabutyl ammonium salts, tetramethyl ammonium salts, tetraethyl ammonium salts, methylpyridinium salts, ethylpyridinium salts, butylpyridinium salts, methylquinolinium salts, ethylquinolinium salts and butylquinolinium salts of tetraphenylboron, tetranaphthylboron, tetrabiphenylboron, tetrakis(p-chlorophenyl)boron, tetrakis(p-fluorophenyl)boron, tetrakis(p-methoxyphenyl)boron, tetrakis(m-methoxyphenyl)boron, tetrakis(p-ethoxyphenyl)boron, tetrakis(m-ethoxyphenyl)boron, tetrakis(p-butoxyphenyl)boron, tetrakis(m-butoxyphenyl)boron, tetrakis(p-methylphenyl)boron, tetrakis(m-methylphenyl)boron, tetrakis(p-ethylphenyl)boron, tetrakis(m-ethylphenyl)boron, trialkyl(p-butyl-

phenyl)boron, tetrakis(m-butylphenyl)boron, tetrakis(3,5-bistrifluoromethyl)phenylboron and tetrakis[3,5-bis(1,1,1,3,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]boron (hereinafter, alkyl group is n-butyl, n-octyl, n-dodecyl or the like).

The above aryl borates may be used alone or in admixture of two or more.

5 Known transition metal compounds may be used as the component (D) contained in the dental primer of the present invention. Specific examples of the transition metal compound include bromides such as vanadium bromide, nickel bromide, copper bromide, iron bromide and cobalt bromide; chlorides such as nickel chloride, vanadium chloride, palladium chloride, nickel chloride, titanocene dichloride, titanium chloride, iron chloride and cobalt chloride; fluorides, such as vanadium fluoride, cobalt fluoride, copper fluoride, nickel fluoride and potassium titanium fluoride; sulfates such
10 as palladium sulfate, nickel sulfate, titanium sulfate, copper sulfate, iron sulfate and cobalt sulfate; nitrates such as nickel nitrate, palladium nitrate, nickel nitrate, iron nitrate and cobalt nitrate; inorganic acid salts such as phosphates exemplified by iron diphosphate and cobalt phosphate; organic acid salts such as nickel acetate, copper acetate, cobalt acetate, cobalt benzoate, copper citrate, iron citrate, potassium titanium oxalate, iron oxalate, cobalt oxalate, iron lactate, iron fumarate, copper acrylate, copper methacrylate, nickel sulfamate, vanadium oxide stearate, cobalt stearate,
15 vanadium naphthenate, cobalt naphthenate and cobalt gluconate; hydroxides such as palladium hydroxide, nickel hydroxide, iron hydroxide, copper hydroxide and cobalt hydroxide; and organic complexes with acetylacetone such as vanadium acetyl acetonate, nickel acetylacetonato, copper acetylacetonato, iron acetylacetonato and cobalt acetylacetonato or with EDTA. Transition metals contained in these transition metal compounds may have any valence. Out of these transition metal compounds, iron, cobalt and copper compounds are preferred and iron and copper compounds are particularly preferred. The transition metal compounds may be used alone or in combination.

The primer composition of the present invention comprising the above components (A), (B), (C) and (D) preferably comprises 5 to 55 % by weight of the polymerizable monomer containing an acidic group (A), 0.1 to 20 % by weight of the aryl borate (C), 0.0001 to 20 % by weight of the transition metal compound (D) and the remainder which is water (B), based on the total weight of these components.

25 When the polymerizable monomer containing an acidic group (A) is used in a proportion of from 5 to 55 % by weight, the primer composition exhibits excellent adhesive force to the tooth, while the polymerizable monomer containing an acidic group (A) is preferably used in a proportion of from 5 to 25 % by weight. When the proportion is less than 5 % by weight, adhesive force to the enamel is liable to reduce and when it is more than 25 % by weight, the adhesive strength to the dentin is liable to lower.

30 The proportion of the aryl borate (C) is preferably 0.1 to 20 % by weight, more preferably 0.2 to 15 % by weight, the most preferably 0.5 to 10 % by weight.

The proportion of the transition metal compound (D) is preferably 0.0001 to 20 % by weight, more preferably 0.02 to 10 % by weight, particularly preferably 0.1 to 5 % by weight. When the proportion is less than 0.0001 % by weight, the effect is small, while when it is more than 20 % by weight, the adhesive strength lowers.

35 The proportion of water (B) is the remainder of the total which is 100 % by weight. That is, since the proportion of water changes according to the proportions of other components, it is not particularly limited. To demineralize the enamel and obtain mechanical retention, water is preferably contained in a proportion of not less than 5 % by weight, more preferably not less than 20 % by weight, whereby sufficient adhesive force can be obtained.

40 The primer composition of the present invention can further contain an organic solvent (E) when the polymerizable monomer containing an acidic group (A) is difficult to dissolve in water. That is, it is also possible to use the primer composition after dissolving all the components using an organic solvent to prepare a homogeneous solution or an emulsion of such an extent that it does not cause a problem when in use.

Specific examples of the organic solvent include alcohols and ethers such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, propanediol, butanediol, pentanediol, hexanediol, butenediol, glycerine, trimethylolpropane,
45 hexanetriol, allyl alcohol, ethylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol, triethylene glycol monomethyl ether, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 2-methoxyethanol, 2-ethoxyethanol, 2-(methoxyethoxy)ethanol, 2-isopropoxyethanol, 2-butoxyethanol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, dipropylene glycol, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether and glycerine
50 ether; ketones such as acetone and methyl ethyl ketone; carboxylic acids such as acetic acid, acetic anhydride and propionic acid; and the like. Solvents having a polymerizable functional group such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, and N-methylol (meth)acryl amide may also be used.

Out of these, the preferred are solvents which have little harmful effect on vital function, such as ethanol, isopropanol, propanediol, butanediol, pentanediol, glycerine, trimethylolpropane, hexanetriol, aryl alcohol, ethylene glycol, ethylene
55 glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol, triethylene glycol monomethyl ether, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, dipropylene glycol, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, glycerine ether, acetone, 2-hydroxyethyl methacrylate and the like.

The above organic solvents may be used in admixture of two or more as required.

In the primer composition containing the organic solvent (E) of the present invention, the weight proportions of the components (A), (C), (D) based on the total weight of the components (A), (B), (C), (D) and (E) are the same as the primer composition comprising the components (A), (B), (C) and (D), and the proportion of the organic solvent as the component (E) is 1 to 80 % by weight and the water (B) occupies the remainder.

The primer composition of the present invention may contain other polymerizable monomer, water-insoluble organic solvent, polymerization catalyst other than aryl borates, polymerization inhibitor, pigment, inorganic and organic fillers in amounts that do not impair performance thereof.

Examples of the other polymerizable monomer include monofunctional polymerizable monomers such as methyl methacrylate, ethyl methacrylate, tetrahydrofurfuryl methacrylate, 2-hydroxyethyl methacrylate, N-methylolmethacrylamide and acrylates thereof; aromatic difunctional monomers such as 2,2-bis(4-methacryloyloxyphenyl)propane, 2,2-bis(4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl)propane, 2,2-bis(4-methacryloyloxyethoxyphenyl)propane, 2,2-bis(4-methacryloyloxydiethoxyphenyl)propane, 2,2-bis(4-methacryloyloxytetraethoxydiphenyl)propane, 2,2-bis(4-methacryloyloxy-pentaethoxyphenyl)propane, 2,2-bis(4-methacryloyloxydipropoxyphenyl)propane, 2(4-methacryloyloxyethoxy)phenyl-2-(4-methacryloyloxydiethoxyphenyl)propane, 2(4-methacryloyloxydiethoxyphenyl)-(4-methacryloyloxytriethoxyphenyl)propane, 2(4-methacryloyloxydipropoxyphenyl)propane, 2,2-bis(4-methacryloyloxyisopropoxyphenyl)propane, 2,2-bis(4-methacryloyloxyisopropoxyphenyl)propane and acrylates corresponding thereto; aliphatic difunctional monomers such as ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, butylene glycol dimethacrylate, neopentyl glycol dimethacrylate, propylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, and acrylates corresponding to these; trifunctional monomers such as trimethylol propane trimethacrylate, trimethylol ethane trimethacrylate, trimethylolpropane trimethacrylate, and acrylates corresponding to these; tetrafunctional monomers such as pentaerythritol tetramethacrylate and pentaerythritol tetraacrylate; and the like.

Examples of the water-insoluble organic solvent include hexane, butane, octane, toluene, dichloromethane, chloroform, carbon tetrachloride, dichloromethane, trichloroethane, methyl ethyl ketone, pentanone, ethyl formate, propyl formate, butyl formate, ethyl acetate, propyl acetate, butyl acetate and the like.

Examples of the polymerisation catalyst other than aryl borates include organic peroxides such as d-t-butyl peroxide, dicumyl peroxide, lauroyl peroxide and benzoyl peroxide; azo compounds such as azobisisobutyronitrile; sulfinic acid salts such as sodium benzenesulfinate, sodium p-toluenesulfinate, sodium m-nitrobenzenesulfinate and sodium p-fluorobenzenesulfinate; barbituric acids such as 5-butylbarbituric acid and 1-benzyl-5-phenylbarbituric acid; and the like. Examples of the polymerization catalyst which generates a radical with light include α -diketones such as camphorquinone, benzyl, α -naphthyl, acetophenone and naphthoquinone; thioxanthenes such as 2,4-diethylthioxanthone and 2-chlorothioxanthone; and optical initiators such as 2-benzyl-dimethylamino-1-(4-morpholinophenonyl)butanone-1, and the like. Promoters for the above optical initiators include, for example, tertiary amines such as N,N-dimethylaniline, N,N-dimethylamino-p-toluidine, ethyl N,N-dimethylamino-p-benzoate, isoamyl N,N-dimethylamino-p-benzoate and N,N-dimethylamino-p-acetophenone; and amino acids such as N-phenylglycine.

As for the package of the dental primer of the present invention, the aryl borate is preferably packaged separately from the polymerizable monomer containing an acidic group and the transition metal compound because they are blended right before use. Since the aryl borate generates a radical under an acidic condition thereby to decompose, it need be packaged separately from the polymerizable monomer containing an acidic group as an acid component and the transition metal compound. For example, it is preferred that a solution containing the polymerizable monomer containing an acidic group, the transition metal compound and the organic solvent as main ingredients and a solution containing water and an aryl borate as main ingredients should be prepared, packaged separately and mixed together right before use.

As for bonding operation using the dental primer of the present invention, this primer is applied to the surface of a tooth using a sponge or brush, left for a few seconds to a few minutes and thereafter dried by air blowing. Then, an adhesive is applied to the pretreated surface of the tooth, various repair materials are brought into contact with the surface, and the adhesive is cured by polymerization to make the crown material to be firmly bonded to the tooth.

The dental primer of the present invention may be divided for use. For example, after the surface of a tooth is pretreated with an aqueous solution of the transition metal compound, it may be treated with an organic solution of the polymerizable monomer containing an acidic group and the aryl borate. In this case, it is considered that the primer composition of the present invention is formed on the surface of the tooth.

The aryl borate used in the primer composition of the present invention is useful as a catalyst for the polymerization of a polymerizable monomer when it is used in combination with the transition metal compound and the acidic compound. All the polymerizable monomers listed above are used as the polymerizable monomer. The acidic compound can be such a polymerizable monomer containing an acidic group as described above, but may be an inorganic acid such as hydrochloric acid, phosphoric acid, nitric acid or sulfuric acid; an organic acid such as citric acid, maleic acid, malonic acid, acetic acid, oxalic acid, butyric acid, succinic acid, fumaric acid, benzoic acid or benzenesulfonic acid; and further, an acidic compound such as a compound which is used as an optically cationic polymerization catalyst and

generates an acid when it is exposed to light is also usable.

According to the present invention, there are also provided catalyst components for the polymerization of a polymerizable monomer, which comprise a combination of an aryl borate and a transition metal compound, such as catalyst components for polymerizing a dental composition comprising a polymerizable monomer, and a polymerization catalyst containing these polymerization catalyst components and an acidic compound, such as a polymerization catalyst for a dental composition comprising a monomer containing an acidic group.

The dental primer composition of the present invention can exhibit high adhesive strength to both dentin and enamel not only when an optically polymerizable adhesive is used but also when a chemically polymerizable adhesive is used in the bonding of a crown repair material to the tooth.

Examples

The following examples are given to further specifically illustrate the present invention. However, it is to be understood that the present invention is in no way limited by these examples. Compounds and their abbreviations used in the specification and examples are given below.

(1) abbreviations and structures

Phenyl-P: 2-methacryloyloxyethylphenyl hydrogen phosphate

PM: 2-methacryloyloxyethyl dihydrogen phosphate

PM-2: bis(2-methacryloyloxyethyl)hydrogen phosphate

MAC-10: 11-methacryloyloxy-1,1-undecanedicarboxylic acid

MTS: 2-methacryloyloxyethyl 3'-methacryloyloxy-2'-(3,4-dicarboxybenzoyloxy)propyl succinate

EGDME: ethylene glycol dimethyl ether

EGMEA: ethylene glycol monomethylether acetate

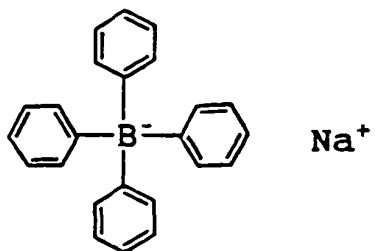
EGEEA: ethylene glycol monoethyl ether acetate

BPO: benzoyl peroxide

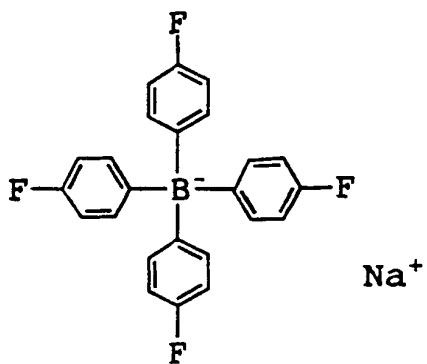
DMPT: N,N-dimethyl-p-toluidine

CQ: camphorquinone

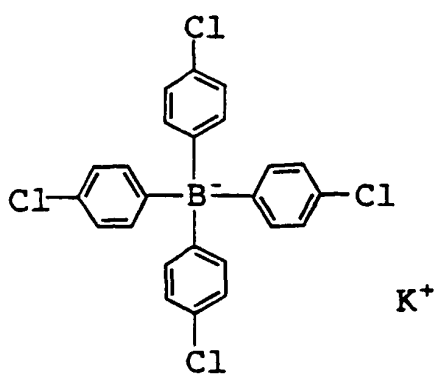
PBNa;



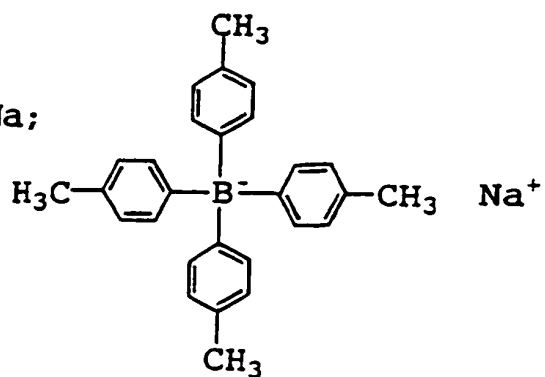
FPBNa;



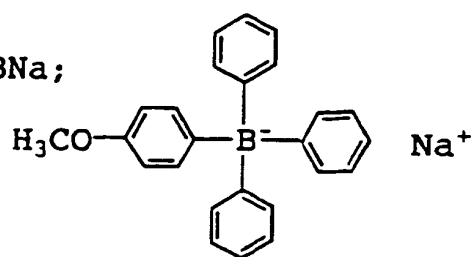
CIPBK;



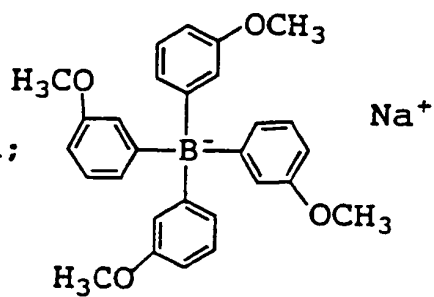
5 4p-MPBNa;



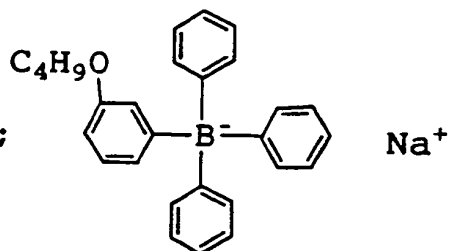
20 p-MEPBNa;

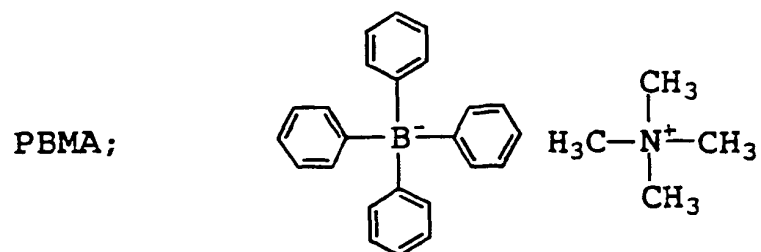
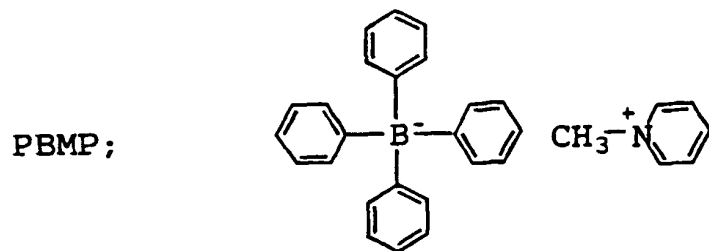
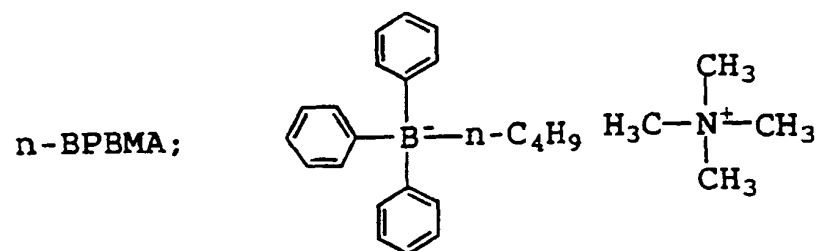
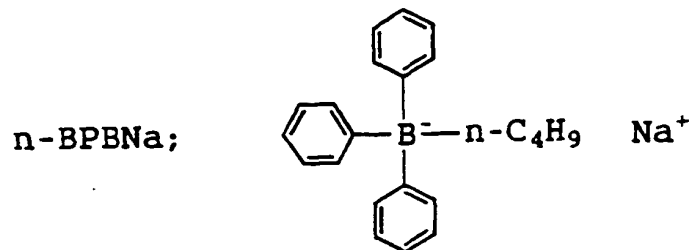
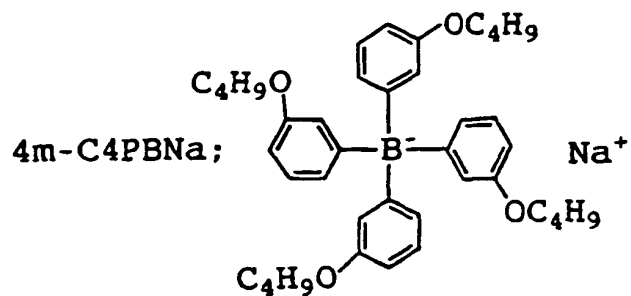


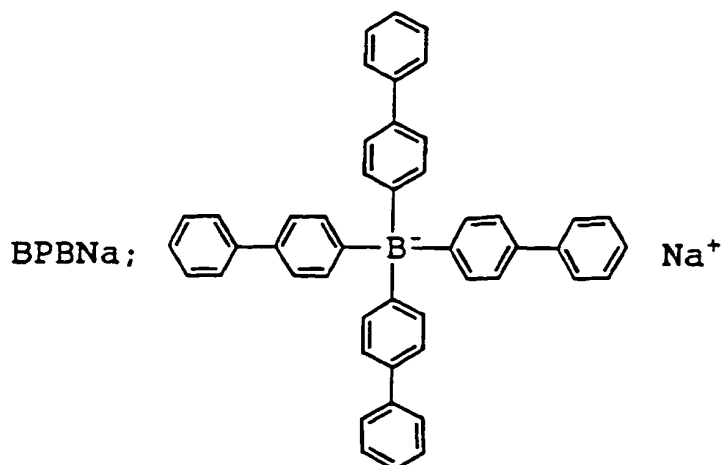
35 4m-MEPBNa;



45 m-C4PBNa;





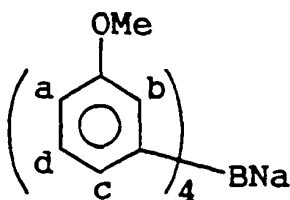


20 The aryl borate used in the present invention can be synthesized by a known method, but an example thereof is shown below.

Production Example 1

25 1.46 Grams (0.06 mol) of metal magnesium and 10 ml of tetrahydrofuran (THF) dried in advance were charged in a 300 ml three-necked flask, and stirred at room temperature for 30 minutes in a nitrogen atmosphere. To this solution was added small amounts of iodine and 1,2-dibromoethane dropwise. Thereafter, 9.352 g (0.05 mol) of 3-bromoanisole was added dropwise to the resulting mixture slowly using a dropping funnel under cooling with ice. After dropping, the mixture was refluxed for 1 hour and then, it was left to stand until its temperature became room temperature. To this reaction solution was dropwise added 1.70 g (0.012 mol) of a trifluoroborane diethyl ether complex and then, refluxed for 1 hour. After having left it stand, 200 ml of an aqueous solution containing 18 g (0.45 mol) of sodium hydroxide was added thereto. After stirring the solution at room temperature for 1 hour, sodium chloride was added to the reaction solution for saturation to separate a water layer. The separated water layer was extracted twice using 150 ml of THF. After an organic layer was dried over sodium sulfate, the solvent was distilled off under a reduced pressure. The obtained solid was recrystallised from hexane to give 3.60 g of a white solid which was an object product of tetrakis(m-methoxyphenyl)borate sodium. The result of NMR (d₆DMSO) analysis is shown below.

35 NMR (δ, ppm): 3.6 (3H, -OCH₃),
6.4 (1H, a)
40 6.7 (1H, b, c),
6.8 (1H, d).



The adhesive strength was evaluated in accordance with the following test method.

(2) Measurement method of adhesive strength

Pretreatment method:

5 A bovine front tooth was removed within 24 hours after slaughter and the surface of the enamel or dentin was abraded to expose with #800 Emery paper under injection of water so as to become flush with the surface of a lip. Thereafter, the surface was dried by a blow of compressed air for about 10 seconds, and a double-sided adhesive tape having a 4 mm-diameter hole was fixed to this flat surface to define an adhesion area. The dental primer of concern was applied thinly to this area, left for 30 seconds and dried by a blow of compressed air for about 10 seconds.

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Bonding with an optically curable adhesive:

The MACBOND bonding material (a product of Tokuyama Corporation.) which was an optically curable adhesive was applied to the adhesion surface prepared by the above method, and cured by irradiation using a POWER LIGHT (a product of Tokuyama Corporation.) for 10 seconds. Thereafter, a 4 mm-thick wax having a 6 mm-diameter hole was adhered to the double-sided tape concentrically to prepare a mimic cavity. The PALFIQUE LITEPOSTERIOR (a product of Tokuyama Corporation.), which was a photocurable composite resin, was filled into this mimic cavity. The mimic cavity was covered by a polypropylene sheet and irradiated with light for 30 seconds to polymerize to cure the composite resin to prepare a test sample. This test sample was immersed in water at 37°C for 24 hours and thereafter, subjected to a tensile test at a cross head speed of 10 mm/min using a tensile tester (AUTOGRAPH supplied by Shimadzu Corp.).

20

Bonding with a chemically curable adhesive:

The BISTITE RESIN CEMENT (a product of Tokuyama Corporation.) which was prepared by kneading two different pastes on a mixing pad for 10 seconds to obtain a uniform mixture was applied to the pretreated adhesion area and an 8 mm-diameter stainless steel attachment was contacted under pressure to the cement to prepare a test sample. This test sample was kept at 37°C in a humid atmosphere for 1 hour, immersed in water at 37°C for 24 hours and then, measured for its tensile adhesive strength at a cross head speed of 10 mm/min using a tensile tester (Autograph AG5000 of Shimadzu Corp.).

25

Four adhesion test samples were measured for each test and an average value of the measurement values was taken as adhesive strength.

Example 1

35 A solution A consisting of 0.5 g of Phenyl-P, 1.5 g of PM and 10 mg of copper (II) citrate (1/2) hydrate and a solution B consisting of 0.3 g of mPBNA and 7.7 g of water were mixed together right before use to prepare an uniform suspension. This suspension was used as a primer to treat the surface of a tooth, and bonding operation was carried out using the BISTITE RESIN CEMENT. Adhesive strength when a chemically polymerizable adhesive was used was measured. The results are shown in Table 1. The adhesive strength to the dentin was 10.5 MPa and the adhesive strength to the enamel was 17.2 MPa.

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Example 2

A solution A consisting of 1.5 g of Phenyl-P, 1.0 g of MTS, 10 mg of copper (II) citrate (1/2) hydrate and 1.5 g of EGDME and a solution B consisting of 5.7 g of water and 0.3 g of TPhBNA were mixed together right before use. The resulting solution was used as a primer to treat the surface of a tooth, bonding operation was carried out using the BISTITE RESIN CEMENT, and the adhesive strength was measured. The results are shown in Table 1. The adhesive strength to the dentin was 12.9 MPa and the adhesive strength to the enamel was 18.3 MPa.

50 Examples 3 to 35

Primers were prepared in the same manner as in Example 2, and bonding operation was carried out using the BISTITE RESIN CEMENT. The compositions of the primers and the adhesive strengths to the dentin are shown in Tables 1 to 4. Examples 3 to 10 are cases where the kind and amount of the polymerizable monomer containing an acidic group contained in the primers used were changed. Examples 11 to 17 are cases where the kind and amount of the transition metal compound were changed and Examples 18 to 21 are cases where the kind of the organic solvent was changed. Examples 22 to 33 are cases where the kind and amount of the aryl borate were changed and Examples 34 and 35 cases where the amount of water was changed. In all the cases, excellent adhesive strength was obtained.

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Table 1

Ex. No.	Primer composition (parts by weight)						Adhesive strength to dentin (MPa)	Adhesive strength to enamel (MPa)
	(A) polymerizable monomer containing acidic group	(D) transition metal compound	(E) organic solvent	(C) aryl borate	(B) water			
1	Phenyl-P PM 15	Copper citrate 0.1	-	PBNa 3	77		10.5	17.2
2	Phenyl-P MTS 10	Copper citrate 0.1	EGDME 15	PBNa 3	57		12.9	18.3
3	Phenyl-P MAC-10 4	Copper citrate 0.1	EGDME 31	PBNa 3	57		13.4	17.8
4	Phenyl-P 15	Copper citrate 0.1	EGDME 25	PBNa 3	57		10.3	16.7
5	PM-2 MTS 10	Copper citrate 0.1	EGDME 20	PBNa 3	57		10.8	16.6
6	PM-2 PM 6 MAC-10 5	Copper citrate 0.1	EGDME 25	PBNa 3	57		12.3	19.9
7	PM-2 PM 6 MTS 10	Copper citrate 0.1	EGDME 15	PBNa 3	57		11.4	18.2
8	PM-2 PM 10.8 7.2	Copper citrate 0.1	EGDME 22	PBNa 3	57		10.0	17.2

Ex. : Example

Table 2

Ex. No.	Primer composition (parts by weight)							Adhesive strength to dentin (MPa)	Adhesive strength to enamel (MPa)		
	(A) polymerizable monomer containing acidic group	(D) transition metal compound	(E) organic solvent	(C) aryl borate	(B) water						
9	Phenyl-P MTS	10 10	Copper acetate	0.1	EGDME	20	PBNa	1	59	12.0	20.6
10	Phenyl-P MAC-10	10 8	Copper (II) chloride	0.1	EGDME	22	PBNa	1	59	10.6	17.3
11	Phenyl-P MTS	15 10	Cobalt acetyl acetate	0.1	EGDME	15	PBNa	3	57	10.7	18.4
12	Phenyl-P MAC-10	10 8	Iron acetyl acetate	0.1	EGDME	22	PBNa	3	57	12.3	18.0
13	PM-2 PM	10.8 7.2	Iron (III) chloride	0.4	EGDME	21.6	PBNa	3	57	10.1	17.2
14	Phenyl-P MTS	15 10	Copper citrate	0.02	EGDME	20	PBNa	2	53	10.9	17.1
15	Phenyl-P MTS	10 12	Copper citrate	0.5	EGDME	22.5	PBNa	2	53	11.2	19.1
16	PM-2 PM	9 6	Iron (III) chloride	1.0	EGDME	28	PBNa	3	53	10.5	20.2
17	PM-2 PM	9 6	Copper (III) chloride	3.0	EGDME	26	PBNa	3	53	10.3	18.2

Ex. : Example

Table 3

Ex. No.	Primer composition (parts by weight)										
	(A) polymerizable monomer containing acidic group	(D) transition metal compound	(E) organic solvent	(C) aryl borate	(B) water	Adhesive strength to dentin (MPa)	Adhesive strength to enamel (MPa)				
18	Phenyl-P MTS	15 10	Copper citrate	0.1	EGMEA	19	PBNa	3	53	12.2	16.3
19	Phenyl-P MTS	15 10	Copper citrate	0.1	EGEEA	19	PBNa	3	53	10.3	16.4
20	PM-2 PM MTS	9 6 10	Copper citrate	0.1	EGDMA Acetone	9 10	PBNa	3	53	11.0	17.7
21	PM-2 PM MAC-10	9 6 10	Iron acetyl acetate	0.1	Acetone	19	PBNa	3	53	10.8	18.6
22	Phenyl-P MTS	15 10	Copper citrate	1.0	EGDME	14	FPBNa	3	57	11.5	17.4
23	Phenyl-P MTS	15 10	Copper citrate	0.1	EGDME	15	CIPBK	3	57	10.7	18.4
24	Phenyl-P MTS	15 10	Copper citrate	0.1	EGDME	34	4p-MPBNa	1	40	12.6	18.8
25	Phenyl-P MAC-10	15 10	Copper citrate	0.1	EGDME	17	p-MEPBNa	1	57	12.5	19.3
26	PM-2 PM	10.2 7.8	Iron (III) chloride	3.0	EGDME Acetone	18 20	4m-MEPBNa	3	38	12.0	19.5

Ex. : Example

Table 4

Ex. No.	(A) polymerizable monomer containing acidic group	Primer composition (parts by weight)					Adhesive strength to dentin (MPa)	Adhesive strength to enamel (MPa)
		(D) transition metal compound	(E) organic solvent	(C) aryl borate	(B) water			
27	PM-2 PM 10.2 7.8	Iron (III) chloride 0.6	EGDMA 20 Acetone 11.4	m-C4PBNa 3	47	11.0	18.8	
28	Phenyl-P MTS 15 5	Copper acetate 0.1	EGEEA 20 Acetone 10	4m-C4PBNa	35	11.7	16.1	
29	PM-2 PM MTS 9 6 10	Copper citrate 0.1	EGDMA 18.0	n-BPBNa 2	55	13.6	20.3	
30	PM-2 PM MAC-10 9 6 7	Copper citrate 0.1	Acetone 21	n-BPBNa 2	55	12.2	20.7	
31	Phenyl-P MTS 15 10	Copper citrate 0.1	EGDMA 20 Acetone 17	BPBNa 3	35	10.3	18.2	
32	Phenyl-P MAC-10 15 10	Copper citrate 0.5	EGDME 29.5	PBMP 1	45	10.3	16.5	
33	Phenyl-P MTS 15 10	Copper acetate 0.1	EGDME 35	PBMA 1	39	10.9	18.0	
34	Phenyl-P MTS 15 10	Copper citrate 0.5	EGDME 30 Acetone 18.5	PBNa 1	25	10.3	16.5	
35	Phenyl-P MAC-10 10 10	Copper acetate 0.05	EGDME 20	PBNa 3	67	11.2	18.6	

Ex. : Example

Comparative Examples 1 to 8

Primers were prepared in the same manner as in Example 2, and the adhesive strength to the dentin was evaluated

using the BISTITE RESIN CEMENT. The compositions of the primers and the results are shown in Table 5.

In contrast to the above Examples, Comparative Examples 1 to 4 are cases where one of the aryl borate, transition metal compound, polymerizable monomer containing an acidic group and water as essential components of the present invention lacked, and in all the cases, the adhesive strengths to both dentin and enamel degraded. Comparative Examples 4 and 5 are cases where the constitution proportion of the essential components was outside the range of the present invention, and in all these cases, the adhesive strength to dentin or enamel lowered. Comparative Examples 6 to 8 are cases where other polymerization initiator and/or a promoter were/was used in place of the aryl borate and the adhesive strengths to both dentin and enamel deteriorated in all the cases.

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Table 5

Comp. Ex. No.	Primer composition (parts by weight)						Adhesive strength to dentin (MPa)	Adhesive strength to enamel (MPa)
	(A) polymerizable monomer containing acidic group	(D) transition metal compound	(E) organic solvent	(C) aryl borate	(B) water			
1	Phenyl-P 15 MTS 10	Copper citrate 0.1	EGDME 15	-	60		0	4.2
2	Phenyl-P 15 MTS 10	-	EGDME 15	PBNA 1	35		5.0	10.2
3	-	Copper citrate 0.1	EGDME 40	PBNA 3	55		2.1	3.5
4	Phenyl-P 15 MTS 10	Copper citrate 0.1	EGDME	PBNA 1	-		6.6	5.4
4	PM 35 MAC-10 25	Copper citrate 0.1	EGDME	PBNA 1	5		3.6	4.7
5	Phenyl-P 10 MTS 10	Copper citrate 0.1	EGDME 17	Other catalyst BPO 3	55		0	7.8
6	Phenyl-P 10 MTS 10	Copper citrate 0.1	EGDME 30	Other catalyst DMPT 3	40		1.0	8.0
7	Phenyl-P 10 MTS 10	Copper citrate 0.1	EGDME 40	Other catalyst BPO 3 DMPT 3	39		1.2	9.7
8	Phenyl-P 15 MTS 10	Copper citrate 0.1	EGDME 25	PTsNa 3	47		7.1	17.8

Comp.Ex. : Comparative Example

Example 36

In the same manner as in Example 1, a solution A consisting of 0.5 g of Phenyl-P, 1.5 g of PM and 10 mg of copper

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(II) citrate (1/2) hydrate and a solution B consisting of 0.3 g of PBNa and 7.7 g of water were mixed together right before use to prepare an uniform suspension. The suspension was used as a primer to treat the surface of a tooth, bonding operation was carried out using the MACBOND, and the adhesive strength when an optically curable adhesive was used was measured. The results are shown in Table 6. The adhesive strength to the dentin was 15.2 MPa and the adhesive strength to the enamel was 20.3 MPa.

Examples 37 to 70

Primers were prepared in the same manner as in Examples 2 to 35, and bonding operation was carried out using the MACBOND in place of the BISTITE RESIN CEMENT which is a chemically curable adhesive. The adhesive strengths when an optically curable adhesive was used were measured. The primer compositions and results are shown in Tables 6 to 9.

Excellent adhesive strengths to both dentin and enamel were obtained in all the examples.

Table 6

Ex. No.	Primer composition (parts by weight)						Adhesive strength to dentin (MPa)	Adhesive strength to enamel (MPa)
	(A) polymerizable monomer containing acidic group	(D) transition metal compound	(E) organic solvent	(C) aryl borate	(B) water			
36	Phenyl-P PM 5 15	Copper citrate 0.1	-	PBNA 3	77		15.2	20.3
37	Phenyl-P MTS 15 10	Copper citrate 0.1	EGDME 15	PBNA 3	57		20.7	23.1
38	Phenyl-P MAC-10 5 4	Copper citrate 0.1	EGDME 31	PBNA 3	57		19.8	22.8
39	Phenyl-P 15	Copper citrate 0.1	EGDME 25	PBNA 3	57		17.6	20.9
40	PM-2 10 MTS 10	Copper citrate 0.1	EGDME 20	PBNA 3	57		19.9	20.6
41	PM-2 9 PM 6 MAC-10 5	Copper citrate 0.1	EGDME 25	PBNA 3	57		20.4	21.0
42	PM-2 9 PM 6 MTS 10	Copper citrate 0.1	EGDME 15	PBNA 3	57		18.7	22.3
43	PM-2 10.8 PM 7.2	Copper citrate 0.1	EGDME 22	PBNA 3	57		16.3	20.7

Ex. : Example

Table 7

Ex. No.	Primer composition (parts by weight)						Adhesive strength to dentin (MPa)	Adhesive strength to enamel (MPa)
	(A) polymerizable monomer containing acidic group	(D) transition metal compound	(E) organic solvent	(C) aryl borate	(B) water			
44	Phenyl-P MTS 10 10	Copper acetate 0.1	EGDME 20	PBNa 1	59		21.3	22.4
45	Phenyl-P MAC-10 10 8	Copper (III) chloride 0.1	EGDME 22	PBNa 1	59		18.1	21.6
46	Phenyl-P MTS 15 10	Cobalt acetyl acetate 0.1	EGDME 15	PBNa 3	57		17.5	23.1
47	Phenyl-P MAC-10 10 8	Iron acetyl acetate 0.1	EGDME 22	PBNa 3	57		19.2	21.9
48	PM-2 PM 10.8 7.2	Iron (III) chloride 0.4	EGDME 21.6	PBNa 3	57		16.6	21.6
49	Phenyl-P MTS 15 10	Copper citrate 0.02	EGDME 20	PBNa 2	53		15.8	18.8
50	Phenyl-P MTS 10 12	Copper citrate 0.5	EGDME 22.5	PBNa 2	53		19.6	20.1
51	PM-2 PM 9 6	Iron (III) chloride 1.0	EGDME 28	PBNa 3	53		18.7	22.7
52	PM-2 PM 9 6	Copper (III) chloride 3.0	EGDME 26	PBNa 3	53		17.6	20.4

Ex. : Example

Table 8

Ex. No.	(A) polymerizable monomer containing acidic group	Primer composition (parts by weight)					Adhesive strength to dentin (MPa)	Adhesive strength to enamel (MPa)
		(D) transition metal compound	(E) organic solvent	(C) aryl borate	(B) water			
53	Phenyl-P MTS 15 10	Copper citrate 0.1	EGMEA 19	PBNa 3	53	20.6	20.4	
54	Phenyl-P MTS 15 10	Copper citrate 0.1	EGEEA 19	PBNa 3	53	19.5	21.3	
55	PM-2 PM 9 6 MTS 10	Copper citrate 0.1	EGDMA 9 Acetone 10	PBNa 3	53	20.7	22.6	
56	PM-2 PM 9 6 MAC-10 10	Iron acetyl acetate 0.1	Acetone 19	PBNa 3	53	20.0	21.1	
57	Phenyl-P MTS 15 10	Copper citrate 1.0	EGDME 14	FPBNa 3	57	17.6	19.4	
58	Phenyl-P MTS 15 10	Copper citrate 0.1	EGDME 15	CIPBK 3	57	18.3	20.8	
59	Phenyl-P MTS 15 10	Copper citrate 0.1	EGDME 34	4p-MPBNa 1	40	20.3	22.7	
60	Phenyl-P MAC-10 15 10	Copper citrate 0.1	EGDME 17	p-MEPBNa 1	57	21.3	21.0	
61	PM-2 PM 10.2 7.8	Iron (III) chloride 3.0	EGDME 18 Acetone 20	4m-MEPBNa 3	38	20.6	22.5	

Ex. : Example

Table 9

Ex. No.	(A) polymerizable monomer containing acidic group	Primer composition (parts by weight)					Adhesive strength to dentin (MPa)	Adhesive strength to enamel (MPa)
		(D) transition metal compound	(E) organic solvent	(C) aryl borate	(B) water			
27	PM-2 PM	Iron (III) chloride 0.6	EGDMA 20 Acetone 13.4	m-C4PBNa 1	47	21.6	23.0	
28	Phenyl-P MTS	Copper acetate 0.1	EGEEA 20 Acetone	4m-C4PBNa	35	20.5	22.6	
29	PM-2 PM	Copper citrate 0.1	EGDMA 19.9	PBBNa 1	55	21.2	22.4	
30	PM-2 PM	Iron (III) chloride 0.4	Acetone 21.6	BPBNa 1	55	19.2	21.2	
31	MAC-10							
31	Phenyl-P MTS	Copper citrate 1.0	EGDME 17	BPBB 3	55	17.8	22.3	
32	Phenyl-P MAC-10	Copper citrate 0.5	EGDME 30 Acetone 18.5	m-RPBNa 1	25	20.2	21.4	
33	Phenyl-P MTS	Copper acetate 0.1	EGDME 40	PBNa 1	39	17.3	20.1	
34	Phenyl-P MTS	Copper citrate 0.05	EGDME 25	PBNa 3	47	18.6	19.2	
35	Phenyl-P MAC-10	Copper acetate 0.05	EGDME 20	PBNa 3	67	20.5	23.3	

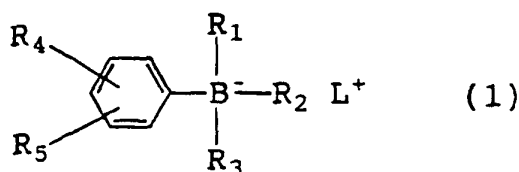
Ex. : Example

Claims

1. A dental primer composition comprising:

- (A) a polymerizable monomer containing an acidic group,
 (B) water,
 (C) an aryl borate, and
 (D) a transition metal compound.

2. The primer composition of claim 1 which comprises 5 to 55 % by weight of the polymerizable monomer containing an acidic group (A), 0.1 to 20 % by weight of the aryl borate (C), 0.0001 to 20 % by weight of the transition metal compound (D) and the remainder being water (B), based on the total of the components (A), (B), (C) and (D).
3. The primer composition of claim 1, wherein the polymerizable monomer containing an acidic group (A) is a polymerizable monomer containing an acidic group selected from the group consisting of a carboxylic acid group, phosphoric acid group, sulfonic acid group and phosphonic acid group.
4. The primer composition of claim 1, wherein the polymerizable monomer containing an acidic group (A) is a polymerizable monomer containing at least one polymerizable group selected from the group consisting of an acryloyl group, methacryloyl group, styryl group, vinyl group and aryl group.
5. The primer composition of claim 1, wherein the aryl borate (C) is represented by the following formula (1):



wherein R_1 , R_2 and R_3 are the same or different and each an alkyl group, alkenyl group, alkynyl group, aryl group, aralkyl group or alkaryl group and may be substituted, R_4 and R_5 are the same or different and each a hydrogen atom, halogen atom, alkyl group which may be substituted or aryl group which may be substituted, and L^+ is a metal ion, quaternary ammonium salt, quaternary pyridinium salt, quaternary quinolinium ion or phosphonium ion.

6. The primer composition of claim 1, wherein the transition metal compound (D) is a halide, organic acid salt, inorganic acid salt or organic complex of a transition metal.
7. The primer composition of claim 6, wherein the transition metal is cobalt or copper.
8. A dental primer composition comprising (A) a polymerizable monomer containing an acidic group, (B) water, (C) an aryl borate, (D) a transition metal compound and (E) an organic solvent.
9. The primer composition of claim 8 which comprises 5 to 55 % by weight of the polymerizable monomer containing an acidic group (A), 0.1 to 20 % by weight of the aryl borate (C), 0.0001 to 20 % by weight of the transition metal compound (D), 1 to 80 % by weight of the organic solvent (E) and the remainder being water (B), based on the total of the components (A), (B), (C), (D) and (E).
10. The primer composition of claim 8, wherein the aryl borate (C) is kept separately from the polymerizable monomer containing an acidic group (A) and the transition metal compound (D) because they are blended before use.
11. Use of a combination of an aryl borate and a transition metal compound as catalyst components for a dental composition.
12. Use of a combination of an aryl borate and a transition metal compound as a catalyst for a dental composition comprising a polymerizable monomer containing an acidic group.
13. A catalyst component for polymerizing a polymerizable monomer, which comprises a combination of an aryl borate and a transition metal compound.
14. A catalyst for polymerizing a polymerizable monomer, which comprises the catalyst component of claim 13 and an acidic compound.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/03739

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ A61K6/083, C08F4/12, 20/26, 20/38, 28/02, 30/02,
C09J4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ A61K6/083, C08F4/12, 20/26, 20/38, 28/02, 30/02,
C09J4/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, 339841, A2 (The Med Corporation), November 2, 1989 (02. 11. 89)	1 - 10
X	& JP, 2-11607, A & US, 4937159, US, 4977511 Refer to synthetic example 1	11 - 14
X	WO, 94/29356, A1 (Idemitsu Kosan Co., Ltd.), December 22, 1994 (22. 12. 94), & EP, 705849, A1 Refer to example 1	13, 14
X	EP, 421659, A2 (The Dow Chemical Company), April 10, 1991 (10. 04. 91) & JP, 3-124706, A & US, A, 5066741 Refer to example 1	13, 14
A	EP, 522456, A2 (Mitsui Toatsu Chemicals, Inc.), January 13, 1993 (13. 01. 93) & CA, 2073145, A & JP, 5-239406, A & US, 5369178, A	1 - 10

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

March 19, 1997 (19. 03. 97)

Date of mailing of the international search report

April 1, 1997 (01. 04. 97)

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